NASA Technical Memorandum 105364

High Molecular Weight First Generation PMR Polyimides for 343 °C Applications

Diane C. Malarik and Raymond D. Vannucci
Lewis Research Center
Cleveland, Ohio

December 1991

HIGH MOLECULAR WEIGHT FIRST GENERATION PMR POLYIMIDES FOR 343 °C APPLICATIONS

Diane C. Malarik and Raymond D. Vannucci
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

E-6742

ABSTRACT

The effect of molecular weight on 343 °C thermo-oxidative stability (TOS), mechanical properties, and processability, of the first generation PMR polyimides was investigated. Graphite fiber reinforced PMR-15, PMR-30, PMR-50, and PMR-75 composites (corresponding to formulated molecular weights of 1500, 3000, 5000, and 7500, respectively) were fabricated utilizing a simulated autoclave process. The data reveals that while alternate autoclave cure schedules are required for the high molecular weight resins, low void laminates can be fabricated which have significantly improved TOS over PMR-15, with only a small sacrifice in mechanical properties.

INTRODUCTION

The polymers research effort at NASA Lewis Research Center, the lead NASA Center for aeropropulsion research, has primarily focused on the development of advanced polymers for aircraft engine applications. In order to improve engine performance, studies have emphasized the use of advanced, lightweight composite materials. Lewis developed the PMR polyimides in order to meet the requirements for high temperature advanced lightweight composites.(1)

Today, PMR-15 is used in a variety of composite engine components currently in production. While present PMR-15 engine applications have resulted in some significant cost and weight savings, they are limited to operating in the 200 to 300 °C temperature regime. Further benefits can be realized by the development of polymer composites with higher temperature capabilities. While the more recently NASA Lewis developed polyimides, such as the second generation PMR polyimide, PMR-II-50, and VCAP-75, are able to withstand higher temperatures, they are significantly more expensive than PMR-15, due to the use of fluorinated monomers.[2,3]

It has long been recognized that the weak link in PMR-15, with regard to its thermo-oxidative stability (TOS), is the nadic ester endcap. By increasing the formulated molecular weight (FMW) of the first generation PMR polyimides, the amount of nadic ester endcap can be significantly reduced. The purpose of this study is to investigate low cost higher molecular weight (HMW) PMR polyimide formulations and their effect on resin and composite processability, physical properties, TOS, and mechanical properties.

EXPERIMENTAL PROCEDURE

Resin Preparation

The monomer reactants used to prepare the resins investigated in this study are shown in Table 1. The NE and MDA were purchased from commercial suppliers, while the BTDE was prepared as a 50 wt % methanol solution by refluxing a suspension of the corresponding dianhydride in methanol until all solids had dissolved, and then for an additional 2 hr.

PMR monomer solutions were prepared at room temperature by dissolving the reactants in methanol to form 50 wt % solid solutions. The stoichiometric ratio of the monomers used was as follows: n mol of BTDE, n+1 mol of MDA, and 2 mol of NE. The resins investigated were PMR-15, PMR-30, PMR-50, and PMR-75. The n values, FMW's, and the weight percent NE of the four resins studied are shown in Table 2.

Neat resin moldings were prepared by heating solutions containing 15 g of solids in an air circulating oven set at 121 °C until all of the solvent had evaporated and the reactants were partially imidized. The dry material was then crushed and the oven temperature increased to 204 °C for 1 hr to complete the imidization to the end-capped prepolymer. The imidized material was then ground into a fine powder. Approximately 4 g was placed into a 5.08 cm (2 in.) diameter die at room temperature. The die was placed into a press preheated to 316 to 343 °C (600 to 650 °F). When the temperature of the die reached 260 °C (500 °F), 6.9 MPa (1000 psi) was applied. Final cure temperature and pressure was maintained for 2 hr. After curing, the moldings were allowed to cool under pressure to 232 °C. At 121 °C, the moldings were removed from the die and post cured in an air circulating oven programmed to heat at 6 °C/min to 260 °C and then 1 °C/min to 371 °C, followed by a 24 hr hold at 371 °C.

Laminate Fabrication

Unidirectional laminates were prepared from BASF's G40-700 graphite reinforced prepreg tape. The tapes were prepared by brush application of resin solutions onto drum wound unidirectional fiber. The prepreg was allowed to dry on the drum to a volatile content of 11 to 12 percent. The prepreg was removed from the drum and cut into twelve 7.62- by 20.3-cm (3- by 8-in.) plies and layed up unidirectionally and bagged according to Fig. 1. The laminates were cured at 343 °C for 2 hr in a simulated autoclave fabrication process in a press. The cure cycle is shown in Fig. 2. All laminates were post cured in nitrogen for 38 hr at 371 °C, according to the post cure cycle shown in Fig. 3.

In addition to the unidirectional laminates, 20 ply PMR-50 and PMR-75 composites reinforced with Celion 3K fabric were prepared. These laminates had thicknesses ranging from 0.70 to 0.81 cm. Photomicrographs of the cross-sections were taken.

Isothermal Aging

Isothermal weight loss measurements were performed on neat resins after exposure to air at 371 °C under both 1 and 4 atm of pressure. A forced air oven was used for 1 atm exposure with an air change rate of 100 cc/min. The air change rate for the 4 atm exposures was five air changes per hour in a 2.0 liter autoclave chamber.

Isothermal weight loss measurements were performed on the unidirectional laminates after exposure to air at 343 °C under 1 atm of pressure. The air change rate in the forced air oven was 100 cc/min. Up to four specimens (2.54 cm by 6.77 cm) of each resin were exposed to 343 °C air, and weighed at various time intervals.

Laminate Evaluation

All unidirectional laminates were C-scanned prior to testing and acid digestion was also performed on the composites to determine volume percent fiber and percent void content.

Mechanical test were performed on post cured laminates at room temperature and at 343 °C. Additional elevated temperature mechanical testing was conducted on specimens after 343 °C exposure. Flexural strength and interlaminar shear strength (ILSS) tests were performed on specimens ranging in thickness from 0.20 to 0.23 cm (0.080 to 0.090 in.). Flexural strength tests were performed on 0.635- by 6.73-cm (0.25- by 2.65-in.) specimens in accordance with ASTM D-790 at a span to depth ratio of approximately 24. ILSS test were performed on 0.635 cm (0.25 in.) wide specimens in accordance with ASTM D-2344 at a span to depth ratio of 5. Elevated temperature tests were performed at 343 °C in an environmental heating chamber. Property values reported are the average of three tests.

RESULTS AND DISCUSSION

Neat Resin Studies

Figure 4 shows the percent of weight loss of the four resins investigated, after 300 hr of exposure to 371 °C, 1 atm air pressure, and after 75 hr of exposure to 371 °C, 4 atm air pressure.[4] The bar chart shows that the PMR-30 and PMR-50 resins, which have comparable thermal stability, show improved TOS over PMR-15. This is due to the lower NE content and thus the lower aliphatic content of the HMW PMR materials. However, at FMW's greater than 5000, there appears to be no improvement in TOS. This is probably due to the lower flow characteristics exhibited by the higher FMW resins, which resulted in resins with higher void levels.

When comparing glass transition temperatures (Tg's) of the four neat resin moldings, as determined by thermal mechanical analysis, we see that the increased TOS comes with a slight sacrifice in Tg, as shown in Fig. 5. This is to be expected, since increasing the FMW increases the length of the chains between the cross-links, thus lessening the amount of cross-linking in the resin, and producing a lower Tg.

Laminate Studies

Ultrasonic C-scanning of the four unidirectional composites revealed that while all laminates were of adequate quality, PMR-15 and PMR-30 resins showed the least amount of void formation. This correlates well with the acid digestion results shown in Table 3. The void content of the PMR-15 laminate was 1.2 percent and increased with increasing FMW up to 4.9 percent for the PMR-75 laminate. The higher void content of the unidirectional PMR-75 laminate suggests that the higher FMW resins require alternate processing parameters due to the low flow characteristic of the higher FMW resins.

This low flow characteristic of the higher FMW resins can be visually observed after processing. Shown in Fig. 6 is the varying amounts of resin flow of six-ply graphite fabric reinforced laminates of the four resin systems studied, after vacuum bag curing at 1.4 MPa (200 psi.) The amount of resin flow during processing decreases significantly with increasing FMW. This correlates well with the volume percent fiber determined for each of the four unidirectional laminates, as shown in Table 3. While the PMR-50 and PMR-75 resins yielded considerably less resin flow, high quality laminates could be successfully fabricated when proper processing parameters were used. The alternate cure schedule for the fabric reinforced PMR-50 and PMR-75 laminates is shown in Fig. 7. Figure 8 shows photomicrographs of the cross sections of 20-ply Celion 3K fabric reinforced PMR-50 and PMR-75 composites, revealing extremely high quality 0.70 cm thick laminates with less than 2 percent voids.

Figure 9 shows the 343 °C TOS of the four unidirectional laminates studied. The TOS of the laminates increases with increasing molecular weight. This is a result of the lower aliphatic content due to the reduction of NE endcap with increasing FMW. However, the data reveals that no further improvements in 343 °C TOS were to be achieved above a FMW of 5000. This is due to the higher void content observed for the unidirectionally reinforced PMR-75 resin laminates.

The glass transition temperatures of the unidirectional laminates after post curing at 700 °C in nitrogen for 38 hr, as measured by rheometric dynamic mechanical analysis, are shown in Fig. 10. The Tg's range from a high of 401 °C for the PMR-15 to a low of 382 °C for the PMR-75. It is apparent that the increasing FMW leads to a reduction in Tg, as would be expected. While the Tg's for the HMW PMR materials are lower than the Tg for PMR-15, they are still well above the 343 °C potential use temperature of the HMW PMR resins.

The improved thermal stability of the HMW PMR does not come without a sacrifice in mechanical properties (Fig. 11). Room temperature flexural strength and interlaminar shear strength decrease with increasing FMW. This is to be expected due to the decreasing amount of cross-linking as FMW is increased. While there is some reduction in these mechanical properties, they are still in the acceptable range for graphite reinforced composites. Although the reduced cross-linking of the HMW PMR resins yield laminates with lower mechanical properties, this reduced amount of cross-linking should result in composites with improved toughness. Studies are currently underway to establish the relationship between toughness and the FMW of PMR resins.

The 343 °C mechanical properties upon aging, shown in Fig. 12, reveal a similar trend. It should be noted that mechanical testing of the PMR-15 unidirectional composite was terminated after 450 hr of 343 °C exposure due to the significant amount of loose surface fiber and its lack of any structural integrity after 740 hr of aging. While the HMW PMR show lower initial mechanical properties, they are maintained for a longer period of time upon 343 °C exposure.

There is also the additional potential benefit of enhanced prepreg storage characteristics which may be exhibited by the higher FMW resins. An earlier study of prepreg storage suggests that lower NE concentrations reduce the rate of formation of mono and bisnadimide during storage.(5) Therefore, HMW PMR materials, which have significantly reduced levels of NE, should show lower levels of mono and bisnadimides after storage.

CONCLUSIONS

The high quality of the fabric reinforced higher FMW resin laminates suggest that these resins can be easily processed into low void laminates using autoclave processing parameters. HMW PMR resin laminates exhibit significantly better TOS over PMR-15 laminates during exposure to 343 °C air. While there is a small sacrifice in initial mechanical properties, the HMW PMR materials maintain these properties for a longer period of time upon 343 °C exposure. HMW PMR resins are a low cost viable alternative for 343 °C applications.

ACKNOWLEDGMENTS

We wish to thank Demetrios S. Papadopoulos for running the acid digestion experiments and Laura Bain, a summer student from the University of Akron, who assisted in the preparation of resin solutions. We also would like to thank Mark Bubnick, a cooperative student from Cleveland State University, for performing the thermal analysis experiments.

REFERENCES

1. Serafini, T.T., Delvigs, P., and Lightsey, G.R., "Thermally Stable Polyimides from Solutions of Monomeric Reactants," Journal of Applied Polymer Science, Vol. 16, No. 4, Apr., 1972, pp. 905-915.

2. Serafini, T.T., Vannucci, R.D., and Alston, W.B., "Second Generation PMR Polyimides," NASA TM X-71894, 1976.

3. Vannucci, R.D., Malarik, D.C., Papadopoulos, D.S., and Waters, J.F., "Autoclavable Addition Polyimides for 371 °C Composite Applications," Advanced Materials: Looking Ahead to the 21st Century, L.D. Michelove, et al., eds., SAMPE, Covina, CA, 1990, pp. 175-185.

4. Vannucci, R.D., "PMR Polyimide Compositions for Improved Performance at 371 °C," SAMPE Quarterly, Vol. 19, No. 1, Oct., 1987, pp. 31-36.

5. Roberts, G.D., and Vannucci, R.D., "Effect of Solution Concentration and Aging Conditions on PMR-15 Resin," SAMPE Journal, Vol. 22, Mar./Apr. 1986, pp. 24-28, 213.

TABLE 1.—MONOMERS USED FOR HMW PMR POLYIMIDE SYNTHESIS

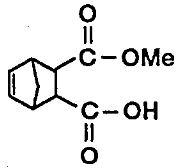
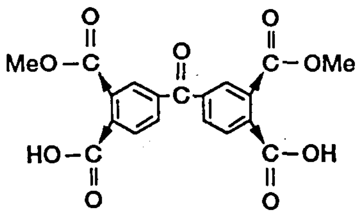
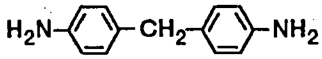
Structure	Name	Abbreviation
	Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	Dimethylester of 3,3′4,4′-benz ophenonetetracarboxylic acid	BTDE
	4,4′-methylenedianiline	MDA

TABLE 2.—HMW PMR RESIN FORMULATIONS STUDIED

[Resin stoichiometry: 2 NE / n BTDE / n+1 MDA.]

Resin	n	FMW	NE, wt %
PMR-15	2.09	1500	21.8
PMR-30	5.19	3000	10.9
PMR-50	9.32	5000	6.5
PMR-75	14.5	7500	4.4

TABLE 3.—UNIDIRECTIONAL HMW PMR COMPOSITE DATA

	PMR-15	PMR-30	PMR-50	PMR-75
Fiber, vol %	59	58	58	51
Voids, percent	1.2	2.0	3.2	4.9

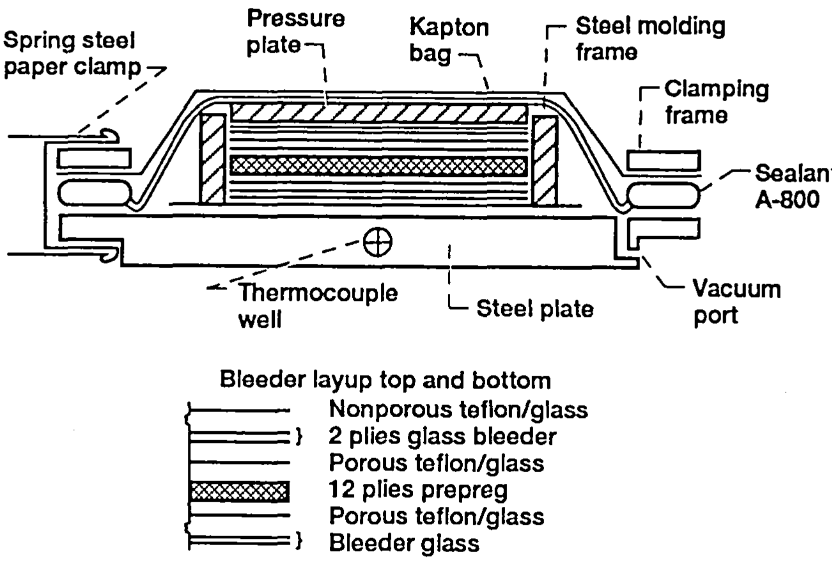


Figure 1.—Vacuum bag system used for autoclave fabrication of HMW PMR composites.

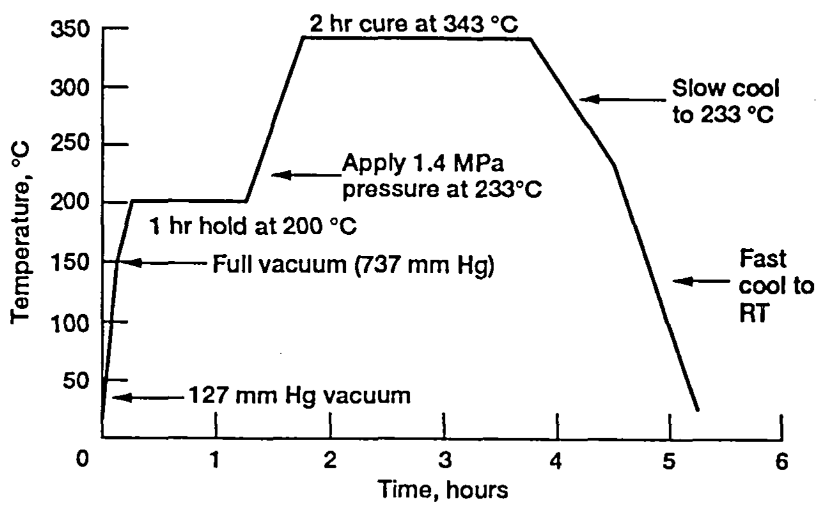


Figure 2.—Autoclave cure cycle for unidirectional HMW PMR composites.

Temp, °C	Ramp/Hold time, hrs
25 to 316	1
Hold at 316	1
316 to 343	1
Hold at 343	2
343 to 371	1
Hold at 371	38
371 to 25	2

Figure 3.—Nitrogen post core cycle for unidirectional HMW PMR composites.

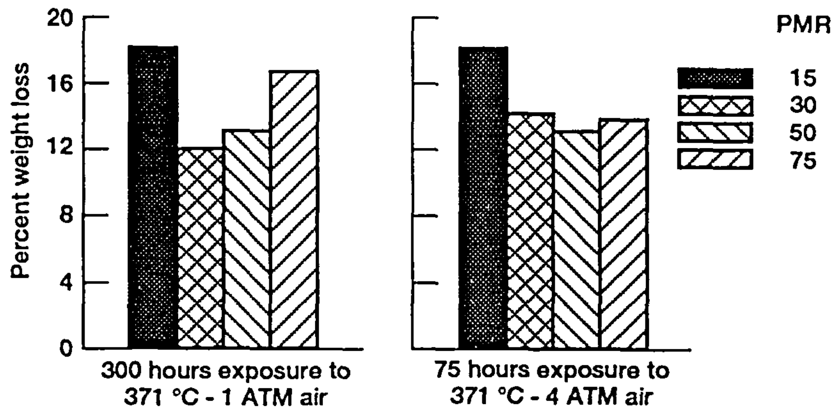


Figure 4.—Thermo-oxidative weight loss, of HMW PMR neat resin after 371 °C air exposure.

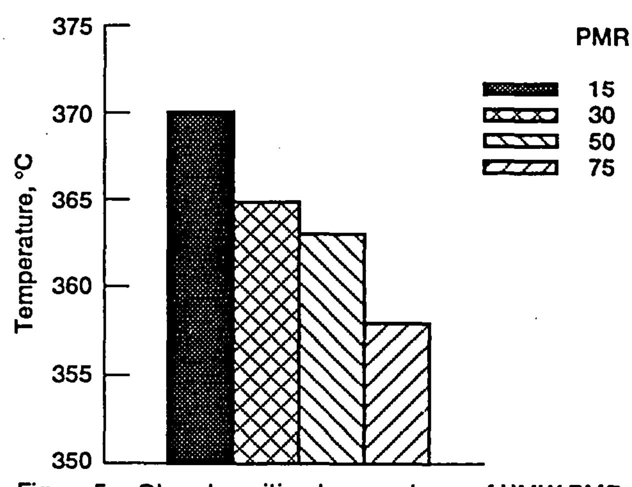


Figure 5.—Glass transition temperatures of HMW PMR neat resin after post curing in air at 371 °C for 25 hours.

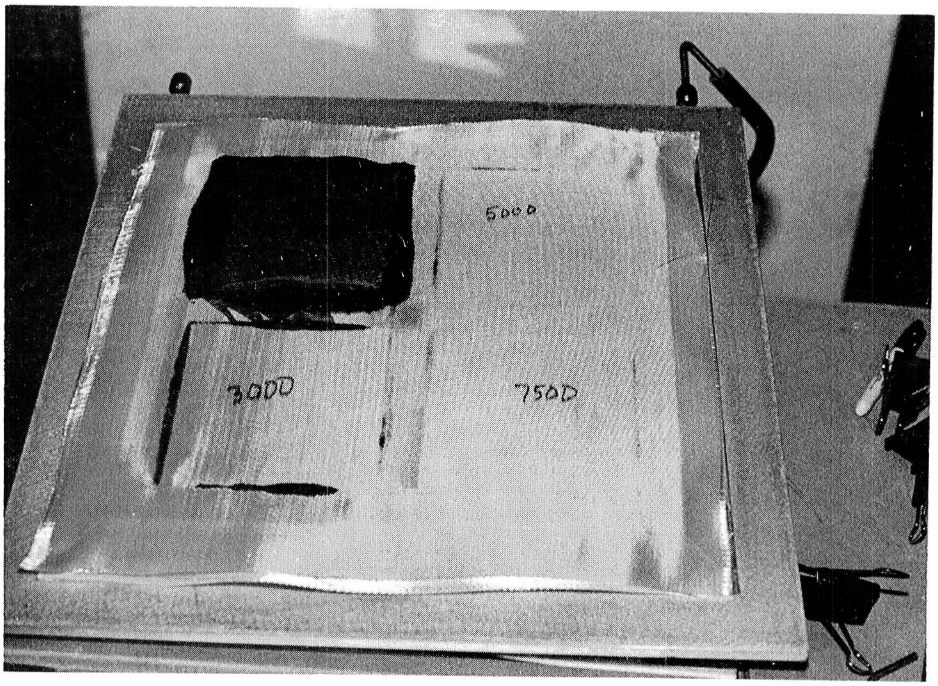


Figure 6.—Photograph of resin flow for various HMW PMR graphite fabric composites after processing.

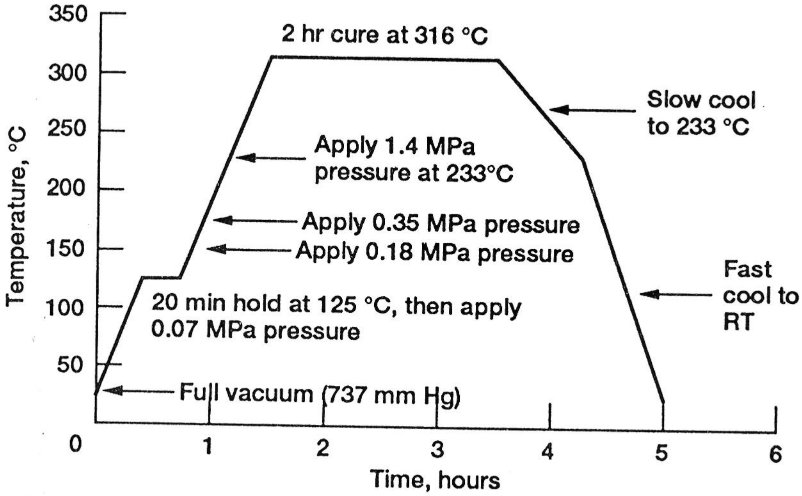
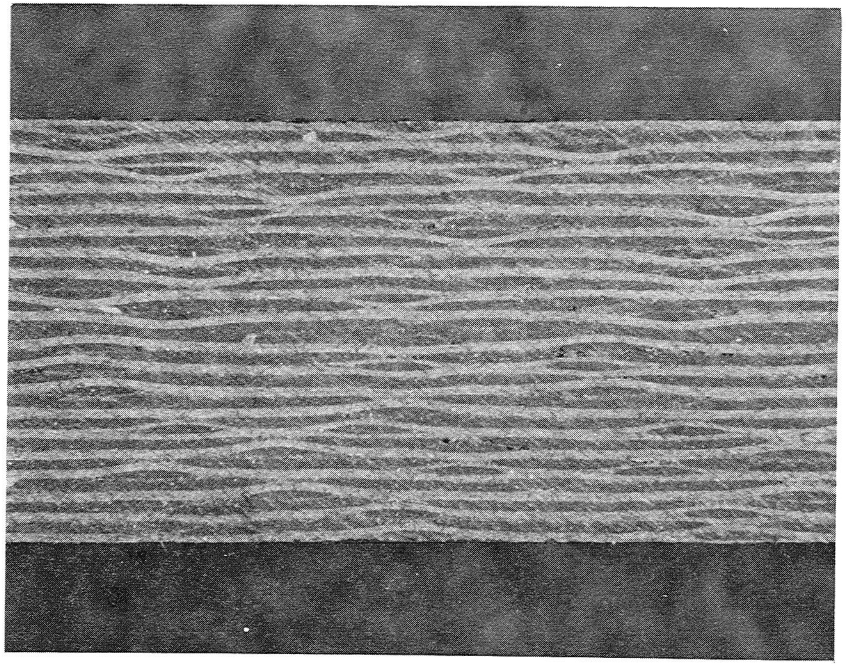
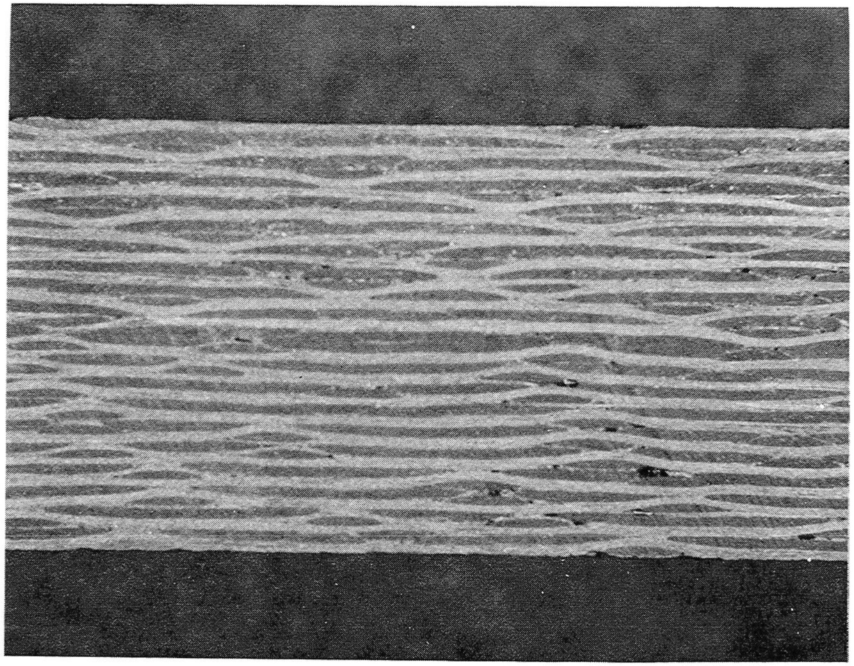


Figure 7.—Autoclave cure cycle for graphite fabric reinforced PMR-50 and PMR-75 composites.



PMR-50/celion 3k fabric



PMR-75/celion 3k fabric

Figure 8.—Photomicrographs of (20 ply) celion 3k fabric reinforced HMW PMR composites, 8.5 x magnification.

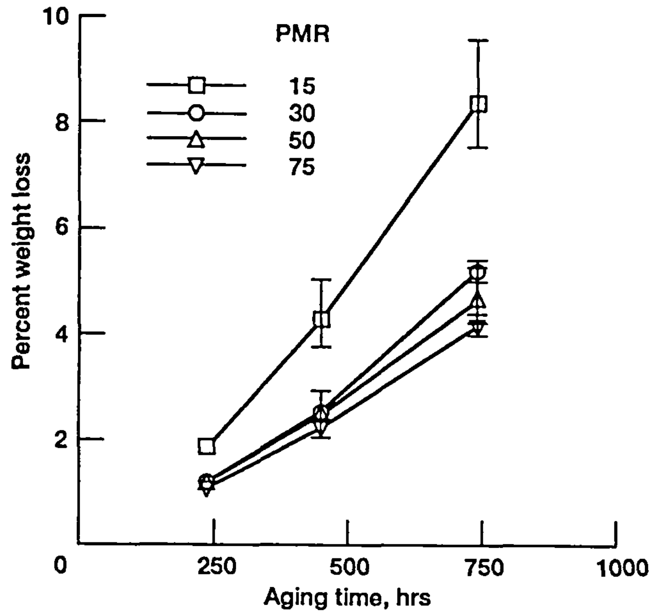


Figure 9.—Thermo-oxidative stability of unidirectional HMW PMR composites during 343 °C air exposure.

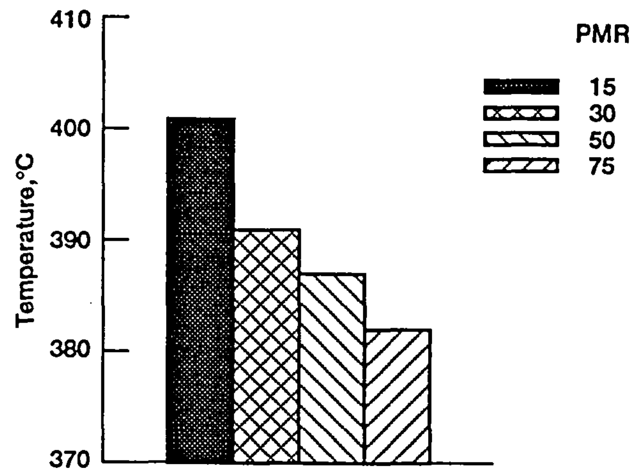


Figure 10.—Glass transition temperatures of unidirectional HMW PMR composites after post curing in nitrogen at 371 °C for 38 hours.

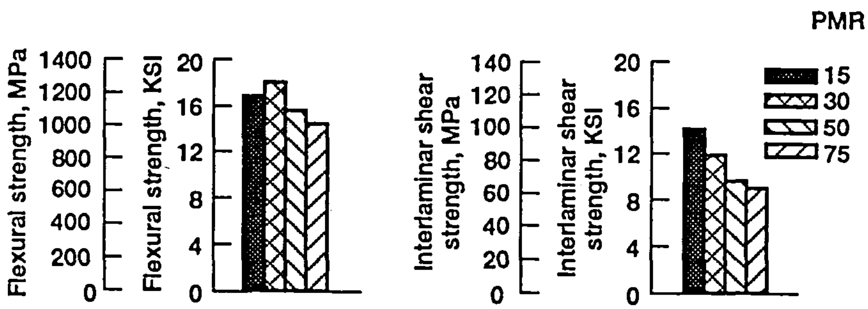


Figure 11.—Initial room temperature mechanical properties of unidirectional HMW PMR composites.

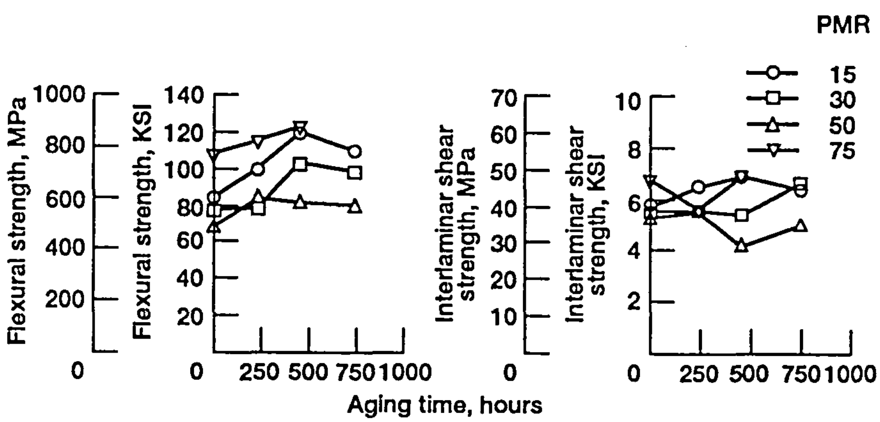


Figure 12.—343 °C mechanical properties of unidirectional HMW PMR composites after exposure to 343 °C air. Aged and tested 343 °C.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	December 1991	Technical Memorandum

4. TITLE AND SUBTITLE

High Molecular Weight First Generation PMR Polyimides for 343 °C Applications

5. FUNDING NUMBERS

WU-510-01-50

6. AUTHOR(S)

Diane C. Malarik and Raymond D. Vannucci

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E-6742

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM-105364

11. SUPPLEMENTARY NOTES

Responsible person, Diane C. Malarik, (216) 433-3203.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 27

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The effect of molecular weight on 343 }C thermo-oxidative stability (TOS), mechanical properties, and processability, of the first generation PMR polyimides was investigated. Graphite fiber reinforced PMR-15, PMR-30, PMR-50, and PMR-75 composites (corresponding to formulated molecular weights of 1500, 3000, 5000, and 7500, respectively) were fabricated utilizing a simulated autoclave process. The data reveals that while alternate autoclave cure schedules are required for the high molecular weight resins, low void laminates can be fabricated which have significantly improved TOS over PMR-15, with only a small sacrifice in mechanical properties.

14. SUBJECT TERMS

Polyimide; High temperature matrix resins; Composites; Graphite fiber; PMR

15. NUMBER OF PAGES 16

16. PRICE CODE A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio 44135

Official Business
Penalty for Private Use $300

FOURTH CLASS MAIL

ADDRESS CORRECTION REQUESTED

U.S.MAIL

Postage and Fees Paid
National Aeronautics and
Space Administration
NASA 451

NASA